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INTERLABORATORY
STUDY 92-2

POLYCYCLIC AROMATIC HYDROCARBON (PAH) STANDARD SOLUTIONS

IN SUPPORT OF

THE INTEGRATED ATMOSPHERIC DEPOSITION NETWORK (IADN)

SEPTEMBER 1992

Ontario

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Our File *Notre reference*

10 June 1994

Ms. Sara Martin
Ontario Ministry of Environment & Energy
Public Affairs & Communications Services Branch
135 St. Clair Ave. West, 2nd Floor
Toronto, Ontario
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Dear Ms. Martin,

In 1992 the Ontario Ministry of the Environment & Energy and the Atmospheric Environment Service (Environment Canada) undertook a joint program of interlaboratory performance evaluation studies in support of the Integrated Atmospheric Deposition Network (IADN). Please find enclosed a copy of the final report for the fourth and final study from 1992: Study 92-2 (Polycyclic Aromatic Hydrocarbons), for your information. Participating laboratories were restricted to those laboratories contributing data to the IADN program or to closely related Air Toxics Programs. All participants were assigned identification codes to maintain confidentiality. Laboratories must be contacted directly for permission to reveal their ID code.

Please contact me at (416) 739-4847 if you have any questions or require additional copies.

Sincerely,

Sylvia Cussion

Sylvia Cussion
Air Toxics Quality Assurance Officer

Canada

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IN SUPPORT OF THE INTEGRATED ATMOSPHERIC DEPOSITION NETWORK (IADN)

SEPTEMBER 1992

Report Prepared by

Sylvia Cussion

for

Quality Management Unit
Laboratory Services Branch
Ontario Ministry of Environment and Energy
PIBS No. 3079

and

Air Quality Research Branch
Atmospheric Environment Service
Environment Canada
ARD Report No. 94-004

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1 SUMMARY OF INTERLABORATORY STUDY 92-2

Interlaboratory Study 92-2 was initiated in support of the Integrated Atmospheric Deposition Network (IADN) to provide an initial assessment of between-laboratory variability for the analysis of Polycyclic Aromatic Hydrocarbons (PAH's). Participation was limited to laboratories which contribute to the IADN database or related programs. This study was sponsored by the Canada-Ontario Agreement (COA) Air Toxics Workgroup, and conducted as a joint project between the Atmospheric Environment Service (AES) of Environment Canada and the Quality Management Unit (QMU), Laboratory Services Branch (LSB) of the Ontario Ministry of Environment and Energy (MOEE).

Six participating laboratories received a set of four ampouled standards that were ready for direct instrumental analysis. The parameter list consisted of 20 different PAH's. Ampoule 1 contained all 20 compounds, while Ampoules 2, 3, and 4 contained subsets of the total target list. Results were received from all of the participants.

The results from this study indicate a low bias relative to the target values for many of the parameters, though at least one participant was close to the target for each parameter. The use of a common reference standard by all of the participants would help determine the accuracy of their standards and improve the consensus among the laboratories.

The variability among the participants differed among the target parameters, with no clear pattern. Co-elution of some compounds contributes to between-laboratory variability and may be an important source of between-laboratory bias for the IADN database. Participants that have only one of a pair of known co-eluting compounds in their calibration standard may be misidentifying a peak in a real sample. Even when correction for misidentified peaks can be made using 50% of the response if both co-eluters are present, some laboratories may still report biased high results while others will report biased low results. If no corrections are made for mis-identified or co-eluting peaks, the value assigned to the unknown peak may consist of contributions from more than one compound. A biased high value for the one target analyte will be that laboratory's contribution to the IADN database.

The need to prepare individual sample sets in different solvents, may also contribute to the between-laboratory variability, due to slight variations in sample preparation and solvent effects. However, compared to the overall analytical variability, this contribution is minor.

The goal of interlaboratory studies such as this is to help participating laboratories identify possible sources of variability and help achieve greater comparability among the participants. As this was the first study of this kind among this group of laboratories, the results provide a starting point from which better agreement can be the goal. Future studies should show improved comparability among the laboratories who participated in this study.

2 INTRODUCTION

Interlaboratory performance studies are conducted to assess the comparability and accuracy of data among different laboratories. These studies are useful for the identification of biases, precision and accuracy problems, as well as ensuring overall data quality. Participation in such studies can serve as a guide for improving individual laboratory performance and maintaining performance standards.

This study was designed to assess the analytical variability among laboratories contributing to the Integrated Atmospheric Deposition Network (IADN). IADN was established as a joint venture between Canada and the United States under the direction of the International Joint Commission[1]. The intent of IADN is to identify toxic airborne substances in the Great Lakes Basin, and by means of the network, quantify the total and net atmospheric loadings of these contaminants, and define spatial and temporal trends in the atmospheric deposition of these substances. Data from several participating agencies is to be merged into a central database. Comparability of these contributing data sets is an important component of the IADN Quality Assurance Implementation Plan[2]. This interlaboratory study provides information to help establish the comparability of data sets. Sponsorship of this interlaboratory study was through the Canada-Ontario Agreement (COA) Air Toxics Workgroup. Funding for the purchase of materials came from the Atmospheric Environment Service (AES) of Environment Canada. Co-ordination and implementation of the study was done by the Quality Management Unit (QMU) of Laboratory Services Branch (LSB) of the Ontario Ministry of Environment and Energy (MOEE).

Interlaboratory Study 92-2 targets laboratories analyzing for Polycyclic Aromatic Hydrocarbons (PAH's) in precipitation and/or ambient air. A target list of 20 PAH's was chosen for this study, comprising target lists from several contributing agencies. The aim of this study was to establish the comparability of instrumental calibration among the participating laboratories. Each participant received a set of ampouled standards ready for direct instrumental analysis. Ampoule 1 contained all of the parameters in the target list, while Ampoules 2, 3, and 4 contained subsets from the target list.

A list of participants is given in Appendix 2. Each participant was assigned a unique identification code for ease in data manipulation.

Section 3 describes sample preparation, sample distribution, analytical methodology, and data evaluation procedures. Final results are tabled in Appendix 1 and discussed in Section 4.

3 PROCEDURE

3.1 Preparation of Ampouled Standards

Neat PAH's of 99% + purity were purchased from Ultra Scientific and Supelco by AES. All subsequent work was done by the QMU of LSB, MOEE. Concentrated stock solutions of each compound were prepared in toluene and sealed into 5 mL amber ampoules. The stock concentrations were between 10 to 15 mg/L and verified using gas chromatography/mass spectrometry analysis by an analytical unit at LSB not involved in analysis of ambient air or precipitation. Ampouled solutions were stored in a freezer at -20°C.

Solutions for the interlaboratory study were prepared from the concentrated stock solutions by diluting appropriate aliquots into a combined solution in toluene. Solution 1 contained all the PAH's on the target list. Solutions 2, 3, and 4 were designed to consist of subsets of the complete target list. The compounds were distributed so that known co-eluters or close eluters were in different solutions. This series of solutions were sealed in 5 mL amber ampoules and labelled IADN1, IADN2, IADN3, and IADN4. They were in a concentration range of μg/mL (See Tables 1-4). This concentration range was suitable only for one of the participants.

To achieve concentration levels that fell in the routine analytical range of the other participants, an aliquot of each of ampoules IADN1, IADN2, IADN3, and IADN4 was diluted to the ng/mL range. Each of the five participants requiring the more dilute solutions required a different solvent for their calibration standards, so separate dilute solutions were prepared in four different solvents. Each participant received a set of four ampoules prepared from the IADN1-4 ampoules, and diluted in the required solvent. The solvents used for each participant are given in Table 5. Each set was at the same concentration level and were labelled IADN1a, IADN2a, IADN3a, and IADN4a.

As each compound was present in two different solutions, one solution had a "low" concentration level and the other a "high" concentration level. All ampoules were stored in a freezer at -20°C until shipped to the participants.

3.2 Sample Distribution

Samples were packed into styrofoam shipping containers and shipped overnight by Purolator Courier to the participating laboratories. A list of the laboratories receiving sample sets is given in Appendix 2. Samples were shipped on September 21, 1992. A copy of all correspondence is also included in Appendix 2.

3.3 Analytical Methodology

Participating laboratories were requested to analyze the samples using their routine in-house methods used to analyze precipitation or ambient air samples for the IADN program. Participants were requested on the report form provided (Appendix 2) to summarize their Instrument and Detector used for the analysis. Information regarding the stationary phase used for separation was requested at a later date. All participants were assigned a unique identification code.

3.4 Data Reporting

Results were submitted to the QMU, LSB in written form. All data were manually entered by laboratory code into an electronic spreadsheet.

The participating laboratories were mailed a copy of the tables of results on January 4, 1993. One participant submitted some notes regarding co-elution results and a possible mis-identification in Ampoule IADN2a. These comments are noted as foot-notes to the tables and in the individual laboratory review.

The interlaboratory mean, median, standard deviation (SD), and relative standard deviation (%RSD) were calculated for each parameter in each of the

"A" series ampoules for which there were 2 or more results reported, and are included in Tables 1-4, Appendix 1. As the data set is small, these calculated values are provided as an approximate indicator of the spread of the data and may not necessarily be statistically correct.

4 DISCUSSION

OVERVIEW OF INTERLABORATORY PERFORMANCE

The between laboratory variability is more difficult to evaluate in this study because of the need to prepare individual solutions for each participant. Conventional interlaboratory study design normally involves the distribution of the same material to all of the participants[4]. While one combined set of solutions was prepared (the IADN1-4 ampoules), only 1 participant analyzed this set of solutions (Laboratory 9225). All of the other participants analyzed their own dilution from this "intermediate" set of solutions. As each participant required a different solvent, five different dilution sets were prepared. This resulted in the possible introduction of preparation errors that could contribute to the overall between-laboratory variability. While every care was taken to minimize preparation errors, slight variations of glassware may have introduced a 1-2% variation among the different solutions.

The differences in solvents may also contribute to between-laboratory variability. As noted in Section 3.1, the individual stock solutions were prepared in toluene, as were the combined solutions (IADN1-4). For Laboratory 9225 analyzing the series IADN1-4, there should have been no solvent effect. For Laboratory 9221, who received their ampoules also in toluene, there also should have been no solvent effect. The other four participants received their solutions prepared in different solvents. Depending on the ampoule, this resulted in 1-8% toluene combined with the other solvent. While only Laboratory 9224 reported a problem with the toluene peak at the front end of their chromatographs, this solvent effect may have affected quantitation of the early eluting compounds for other participants.

As Laboratory 9225 was the only participant to analyze the IADN1-4 series, their performance is discussed separately in the individual laboratory section below. All of the remaining discussion is for the five participants analyzing the "A" series of ampoules.

Two parameters, Benzo(a)fluorene and Benzo(b)fluorene, were on the target list of only one participant. For all other compounds, the interlaboratory mean, median, standard deviation (SD) and relative standard deviation (%RSD) were calculated and included in Tables 1-4. As these calculations were done on a small data set, they are only a very approximate estimate of the data distribution and are not necessarily reliable statistical estimators.

The interlaboratory mean and median were low relative to the target value except for Triphenylene (IADN1a & IADN4a), Dibenzo(a,c)anthracene (IADN1a & IADN2a), Chrysene (IADN1a) and Benzo(e)pyrene (IADN3a). Except for Benzo(e)pyrene, the high bias in these parameters may be attributed to co-elution problems. The distribution of the participants' results relative to the target also indicate an overall low bias (Table 6 and Figure 35). While this may appear to indicate a possible problem in the preparation of the interlaboratory study solutions, for almost all of the parameters in the study, at least one participant agreed with the target (within 10%), though not

always the same participant. For many of the parameters two of the participants agreed with the target, while the other three participants reported lower values. For Acenaphthene (IADN1a & IADN4a), Anthanthrene (IADN1a & IADN3a), and Dibenzo(a,c)anthracene (IADN1a & IADN2a), none of the participants were within 10% of the target. Only two participants reported results for Anthanthrene and Dibenzo(a,c)anthracene, and in both cases, one participant was higher than the target and the other was lower than the target. Further intercomparisons are necessary to establish agreement among the laboratories.

The most common source of bias in an interlaboratory study is a difference in calibration standards. This could be a particular problem for PAH's which are vulnerable to photodegradation. The solutions used in this study were freshly prepared, so there had not been time for any significant degradation to occur between preparation and sample distribution. The age of the participants' calibration solutions was not known, so there may have been some aging effects for an individual participant. This could have contributed to the bias in the interlaboratory study results. While some participants reported results after the requested date (see letter in Appendix 2), all results were reported within 7 weeks of sample shipment. This is well within the normal lifetime of analytical standards (one year), so there should have been no aging of the study solutions. Other sources of between laboratory bias may include the variation in preparation or solvent effect, as noted above.

Another source of between-laboratory variability and difference from the target is the effect of co-elution. This was a potential source of variability particularly in Ampoule IADN1a and IADN1 (Table 1). One laboratory reported co-elution of Benzo(b)fluoranthene and Benzo(k)fluoranthene, two laboratories reported co-elution of Dibenzo(a,c)anthracene and Dibenzo(a,h)anthracene, and four participants had co-elution of Chrysene and Triphenylene. In all cases, the combined result was evenly divided among the two compounds for the purposes of calculating the interlaboratory mean, median and standard deviation. However this may not actually be analytically correct, as the peak area may have been distributed 40-60 between the two compounds, or some other proportion. This may affect the agreement with the target, as well as the between-laboratory variability. Even though 50% of the reported value was used, Chrysene and Triphenylene show high bias by Laboratories 9221 and 9222, but a low bias for Laboratory 9226, with all three laboratories reporting co-elution of the two compounds.

The problem of co-elution also affects correct identification. In Ampoule IADN2a, two participants reported a positive response for Dibenzo(a,h)anthracene, which was not present in that ampoule, but the close or co-eluting Dibenzo(a,c)anthracene was present (Table 2). One of the participants qualified their result after receiving the initial tables of results (see individual laboratory review). Similarly, in IADN4a, Laboratory 9222 reported a positive response for Chrysene, which was not present in that ampoule (Table 4). Triphenylene, which co-elutes with Chrysene, was present in this ampoule. The value reported by this participant should have been identified as Triphenylene, not Chrysene. For the purposes of preparing the Youden plots (see below), Laboratory 9222's reported "Chrysene" result was assigned to Triphenylene for ampoule IADN4a. As well, several participants reported a combined result for Chrysene/Triphenylene in ampoules IADN2, IADN2a, IADN4, and IADN4a when only one of the compounds was present. For the purposes of interlaboratory comparison, the result was assigned to the "correct" parameter. This can only be done in a situation such as an interlaboratory study, where the target compounds are known. In the case of real environmental samples, these laboratories would not be able to

correctly identify the peak unless some other confirmatory technique such as High-Resolution Mass Spectrometry was used.

In all of these cases, the participants were using Gas Chromatography/Mass Selective Detector (GC/MSD) as their analytical technique and detector. The only participant who did not have any co-elution problems was Laboratory 9224, who used High Pressure Liquid Chromatography (HPLC) as their analytical technique. (Laboratory 9223 did not include any of the above co-eluting compounds as part of their target list.)

The selection of GC versus HPLC for the analysis of PAH's may be influenced by various factors. GC is generally used for PAH's up to 24 carbons due to their higher volatility, while HPLC is the choice when PAH's with higher number of carbons are the compounds of interest[5]. (The choice of 24 carbons is somewhat arbitrary.) Larger or more non-volatile PAH's will not elute using GC or may get trapped in the injection port. Several PAH's may also decompose or rearrange pyrolytically to other structures in the high temperature of the GC injection port[5]. These latter reasons support the choice of HPLC. However GC has greater resolving power for the smaller PAH's. Many of the more toxic PAH's fall into this category, influencing the selection of GC as the analytical method. At the time of this study, the IADN program did not specify an analytical method for PAH's. Data produced by the network may indicate a need to specify an analytical method in the future.

As an alternate method of evaluating the results, a graphical technique was used for those parameters with 4 or 5 results from the "A" set of ampoules. As each parameter had a "pair" of results, one from either Ampoule 2, 3, or 4, and the other from Ampoule 1, these results may be plotted on an X-Y plot using the Youden technique[4]. The result from the "low" ampoule is plotted on the vertical axis and the result from the "high" ampoule is plotted on the horizontal axis. The graphs are divided into four quadrants, with the intersection point at the target values. The data points should cluster around the target if random error is the only source of variability. Results in the upper right quadrant are considered biased high and those in the lower left quadrant are biased low. The main source of this type of variability is a difference in analytical standards or inadequate calibration practices. Data points that fall in the lower right or upper left quadrants are considered erratic or out-of-control. Sources of this type of error are more difficult to ascertain. In this study, the participants were analyzing ampoules for direct instrumental injection. Sources of erratic performance could be poor sample injection into the gas chromatograph, a septum leak, poor chromatography if contamination remained from a previous sample, or other instrumental problems. Within-laboratory precision may be assessed by drawing a line between the origin and the intersection of the target values. The closer the data point is to this diagonal line, the better the within-laboratory precision.

The majority of the parameters plotted using the Youden technique (Figures 1 - 15) demonstrate a low bias by most of the participants, though as noted above, at least one participant agreed with the target for almost all of the parameters (except for Acenaphthene, as noted above). In many cases, two of the participants agreed with the target. The low bias may be attributed to a difference in standards between the participants. The majority of results fall on the line drawn between the target and the origin, indicating that most participants demonstrated good within-laboratory precision. The results for Acenaphthylene (Figure 2), Benzo(b)fluoranthene (Figure 5), Benzo(k)fluoranthene (Figure 6), Chrysene (Figure 9), Triphenylene (Figure 10), Fluorene (Figure 12), Phenanthrene (Figure 14) show more erratic performance by the

participants. Variable performance for Chrysene and Triphenylene may be attributed to co-elution effects, as noted above. Further studies would be required to determine the possible source(s) of the within-laboratory precision problems for the other three compounds mentioned above.

INDIVIDUAL LABORATORY PERFORMANCE

Laboratory 9221

Laboratory 9221 noted with their results for IADN4a, that the relative retention time for the peak identified as Chrysene was not acceptable based on their in-house protocol, and suggested that it could be Triphenylene. As noted above in the Overview section, several participants identified the peak in IADN4a as Chrysene or as Chrysene/Triphenylene, when only Triphenylene was present. The reported "Chrysene" values in Ampoule IADN4a for this laboratory (as well as the other participants) was assigned to Triphenylene (see comment above).

One parameter was mis-identified in Ampoule IADN2a. Dibenzo(a,c)anthracene was not on their target list but was present in that ampoule. They identified the peak as Dibenzo(a,h)anthracene, a close eluter to Dibenzo(a,c)anthracene. They did not add any further qualifying comments to their results after receiving the tables or results.

Within-laboratory precision was good for most parameters, though they did have some problems with Anthracene (Figure 3), Benzo(b)fluoranthene (Figure 5), Dibenzo(a,h)anthracene (Figure 8), Chrysene (Figure 9), Triphenylene (Figure 10), and Phenanthrene (Figure 14).

Laboratory 9222

Laboratory 9222 noted with their results that six of the target compounds in the interlaboratory study were not on their target list. Based on their own reference material, they noted that their results for Indeno(1,2,3-c,d)pyrene (on their target list) may have been elevated by the presence of Anthanthracene (not on their target list). Similarly, the presence of Benzo(e)pyrene (not on their target list) could affect their results for Benzo(b)fluoranthene, Benzo(k)fluoranthene, or Benzo(a)pyrene (all on their target list). The presence of Dibenzo(a,c)anthracene (not on their list) could affect their quantitation of Dibenzo(a,h)anthracene (on their list), as well as the presence of Triphenylene (not on their list) could affect their quantitation of Benzo(a)anthracene or Chrysene (on their list). As noted above in the Overview, the "Chrysene" result reported in IADN4a was actually due to the presence of Triphenylene and assigned as such for the purposes of preparing the Youden plot.

When Laboratory 9222 received the table of results, they responded back with some additional notes to their results. In Ampoule IADN1a, the result reported for Chrysene had suspected co-elution with Triphenylene, and the result for Dibenzo(a,h)anthracene had suspected co-elution with Dibenzo(a,c)anthracene. Dividing the reported values between the two co-eluters would bring their results into agreement with the other participants that reported the same co-elution problems (these revisions are noted in Table 1 of this report). In Ampoule IADN2a, they reported a positive result for Dibenzo(a,h)anthracene, which was not present in the ampoule. After checking their chromatograph and mass tables, they feel that the value reported should have been assigned to Dibenzo(a,c)anthracene, which was present in the ampoule.

While these modifications to Laboratory 9222's interlaboratory study data set have been made for the purposes of comparing their results to the other participants, this could not be applied to real samples without the use of additional analytical techniques. Knowledge of historical data may suggest when an individual data point may be anomalous, but modifying that point must be approached with care. By not having both of the known co-eluting compounds in their calibration standard, Laboratory 9222 cannot be certain of the identification of a peak without some other supporting confirmation data. This can lead to biases in a data set, both due to misidentification and attributing a greater value to a compound than is actually present (i.e. quantifying a peak that is a combination of Chrysene and Triphenylene, but assigning the total value only to Chrysene).

They had good agreement with the target values for most of the parameters (Table 6 and Figure 35). Problem parameters were the co-eluting pairs of Chrysene/Triphenylene and Dibenzo(a,c)/(a,h)anthracene, which were biased high. Further method development work may help improve performance for these co-eluting parameters. Within-laboratory precision was good except for Benzo(a)pyrene (Figure 7), Chrysene (Figure 9) and Fluorene (Figure 12).

Laboratory 9223

Laboratory 9223 had the fewest number of compounds in the study on their target list. They were biased low for all their results except Indeno(1,2,3-d,c)pyrene and Phenanthrene in Ampoule IADN2a and Acenaphthylene in Ampoule IADN3a. They also tended to have lower results than most of the other participants, with 60% of their results less than 75% of the target (Table 6 and Figure 35). Comparison of their standards with reference materials should help them improve this bias. They had acceptable within-laboratory precision except for Acenaphthylene (Figure 2), Fluorene (Figure 12) and Phenanthrene (Figure 14).

Laboratory 9224

Laboratory 9224 noted that the presence of toluene in the solutions could have an affect on their results for Acenaphthene and Fluorene. Their original set of results had a very high value reported for Fluorene, that was significantly different from the target and the other participants. Before the results were released, they were contacted and asked to investigate this result. Their original chromatograph showed a very distorted Fluorene peak. For many of the compounds in this study, the levels were higher than their normal analytical range, so that dilution of the ampouled solution may have influenced their original Fluorene result. They repeated the analysis with an undiluted aliquot of Ampoule IADN1a and reported a revised result for Fluorene, which is included in Table 1.

They noted the potential interference for Acenaphthene and Fluorene due to the presence of toluene in the ampoules. Their results for these two compounds were biased low and this may be attributed to the solvent effect.

Laboratory 9224 agreed within 75-110% of the target values for most parameters (Table 6 and Figure 35). In ampoules IADN1a, they had the greatest number of results within 10% of the target for all of the participants (11 out of 18 on their target list). The lack of co-elution problems due to the use of HPLC may contribute to their good performance. They also demonstrated good within-laboratory precision, except for

Fluorene (Figure 12) which can be attributed to the solvent effect as already noted, and Benzo(a)anthracene (Figure 4) and Fluoranthene (Figure 11).

Laboratory 9225

Laboratory 9225 was the only participant to analyze the undiluted IADN1-4 ampoules.

Most of their results were within 75-90% of the target (Table 6 and Figure 35). Their low bias may be attributed to a difference in their calibration standards from the interlaboratory study solutions. Comparison with a reference standard may improve this difference. Problem compounds were Acenaphthene, Acenaphthylene, and Benzo(a)fluorene in Ampoule IADN1, and Dibenzo(a,h)anthracene in IADN1 and IADN4. The low result for Dibenzo(a,h)anthracene is most probably due to co-elution with Dibenzo(a,c)anthracene.

As they had a different target value from the other participants, Laboratory 9225's results could not be included in the Youden plots (Figure 1 - 15) prepared for ampoules IADN1a-4a. A separate set of plots showing Laboratory 9225's within-laboratory precision were prepared (Figures 16 - 34). Within-laboratory precision was good for most parameters except for Chrysene (Figure 26) and Dibenzo(a,c)anthracene (Figure 28).

Laboratory 9226

Laboratory 9226 noted that for their analytical working range, the concentration levels in Ampoules IADN1a, IADN2a, and IADN4a were either at or near their detection limit. They anticipated their analytical precision and accuracy to be poor. While all the participants were consulted by telephone regarding the concentration range appropriate for this study, it is possible that there were some misunderstandings on this point. The concentration levels in Ampoules IADN1-4 (as analyzed by Laboratory 9225) may have been more appropriate for Laboratory 9226.

Many of Laboratory 9226's results were biased low. As noted above, the concentration levels for most of the ampoules were near their detection limits. This may be considered the most likely source for their low bias.

Except for Anthracene (Figure 3), Benzo(b)fluoranthene (Figure 5), Benzo(k)fluoranthene (Figure 6), Benzo(a)pyrene (Figure 7), and Chrysene (Figure 9), they demonstrated good within-laboratory precision. One value for all of these parameters was in the three ampoules that Laboratory 9226 noted as being close to their detection limit. The poorer within-laboratory precision for these parameters may most likely be attributed to the low concentration levels and the associated increase in analytical variability.

5 CONCLUSIONS

The results from this study indicate a low bias relative to the target values for many of the parameters. The use of a common reference standard by all of the participants would help determine the accuracy of their standards and improve the consensus among the laboratories.

The variability among the participants differed among the target parameters, with no clear pattern. Co-elution of some compounds contributes to between-laboratory variability and may be an important source of between-laboratory bias for the IADN database. Participants that have only one of a pair of known co-eluting compounds in their calibration standard may be misidentifying a peak in a real environmental sample. Even when correction for misidentified peaks can be made using 50% of the response if both co-eluters are present, some laboratories may still report biased high results while others will report biased low results. If no corrections are made for mis-identified or co-eluting peaks, the value assigned to the unknown peak may consist of contributions from more than one compound. A biased high value for the one target analyte will be that laboratory's contribution to the IADN database.

The need to prepare individual sample sets in different solvents, may also contribute to the between-laboratory variability, due to slight variations in preparation and solvent effects. However, compared to the overall analytical variability, this contribution is minor.

As this was the first interlaboratory study between this group of participants involved in the IADN program, it serves as a starting point for establishing comparability. Future studies should demonstrate improvements among this group of laboratories.

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5. Fetzer, John C.; 1989. "Gas- and Liquid-Chromatographic Techniques", pp. 59-109, in *Chemical Analysis of Polycyclic Aromatic Compounds*, Tuan Vo-Dinh, editor. John Wiley & Sons.

7 APPENDIX 1 - RESULTS AND GRAPHS

Table 1	Ampoule IADN1 and IADN1a
Table 2	Ampoule IADN2 and IADN2a
Table 3	Ampoule IADN3 and IADN3a
Table 4	Ampoule IADN4 and IADN4a
Table 5	Analytical Conditions
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Figures 1-15	Youden Graphs for Ampoules IADN1a, IADN2a, IADN3a & IADN4a
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Figure 35	Distribution of Participants' Results Relative to the Target

TABLE 1 - Results for IADN1 and IADN1a

AMPOULE/LAB CODE	IADN1	9225	IADN1a	9221	9222	9223	9224	9226	MEAN	MEDIAN	SD	n	%RSD
PARAMETER	µg/mL	µg/mL	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL			
ACENAPHTHENE	0.66	0.48	52.8	40.7	45	43	32.22	44	40.98	43	5.152	5	12.6%
ACENAPHTHYLENE	0.51	0.36	40.8	30.3	40	33	40.74	38	36.41	38	4.559	5	12.5%
ANTHANTHRENE	0.54	NA	43.2	NA	NA	NA	49.86	24	36.93	-	18.286	2	49.5%
ANTHRACENE	0.605	0.50	48.4	43.0	44	NA	45.29	40	43.07	43.5	2.253	4	5.2%
BENZO(A)ANTHRACENE	0.64	0.54	51.2	33.7	46	NA	50.31	32	40.50	39.85	9.037	4	22.3%
BENZO(B)FLUORANTHENE	0.605	0.45	48.4	35.6	45	21	47.86	55 &	40.89	45	13.116	5	32.1%
BENZO(K)FLUORANTHENE	0.7	0.58	56.0	54.4	48	29	58.88	55 &	49.06	54.4	11.872	5	24.2%
BENZO(A)FLUORENE	0.54	0.34	43.2	NA	NA	NA	NC	33	-	-	-	1	-
BENZO(B)FLUORENE	0.755	0.68	60.4	NA	NA	NA	NC	44	-	-	-	1	-
BENZO(A)PYRENE	0.515	0.47	41.2	34.6	33	18	38.78	37	32.26	34.6	8.282	5	25.7%
BENZO(E)PYRENE	0.495	0.50	39.6	43.4	NA	NA	35.77	33	37.39	35.77	5.366	3	14.4%
CHRYSENE	0.51	0.56 *	40.8	57.5 *	66 *	NA	34.95	43 *	50.36	50.25	13.991	4	27.8%
DIBENZO(A,C)ANTHRACENE	0.51	0.50 $	40.8	NA	61.5 $	NA	NC	32 $	46.75	-	20.860	2	44.6%
DIBENZO(A,H)ANTHRACENE	0.715	0.50 $	57.2	64.2	61.5 $	NA	52.35	32 $	52.51	56.925	14.585	4	27.8%
FLUORANTHENE	0.755	0.51	60.4	50.4	50	22	44.38	53	43.96	50	12.670	5	28.8%
FLUORENE	0.64	0.53	51.2	39.2	47	41	52.45 @	43	44.53	43	5.292	5	11.9%
INDENO(1,2,3-C,D)PYRENE	0.545	0.52	43.6	22.4	41	31	49.55	27	34.19	31	10.991	5	32.1%
PHENANTHRENE	0.575	0.44	46.0	40.9	42	39	42.24	39	40.63	40.9	1.570	5	3.9%
PYRENE	0.75	0.65	60.0	54.4	51	22	60.06	50	47.49	51	14.783	5	31.1%
TRIPHENYLENE	0.635	0.56 *	50.8	57.5 *	66 *	NA	49.60	43 *	54.03	53.55	9.943	4	18.4%

NOTES (apply to all 4 data tables)

*	Chrysene and Triphenylene co-elute; half of total assigned to each parameter
#	result reported as combination of Chrysene/Triphenylene; only one compound present in ampoule, so value was assigned to "correct" parameter
##	reported a positive response for Chrysene, which was not included in this ampoule; Triphenylene was present and co-elutes with Chrysene
&	co-elute: half of total value assigned to each parameter
$	co-elute: half of total value assigned to each parameter
@	result qualified: suspect due to peak distortion
**	originally reported as Dibenzo(a,h)anthracene; may have been mis-identified as they co-elute
NA	Not available
NC	Not calibrated for

TABLE 2 - Results for IADN2 and IADN2a

AMPOULE/LAB CODE	IADN2	9225	IADN2a	9221	9222	9223	9224	9226	MEAN	MEDIAN	SD	n	%RSD
PARAMETER	µg/mL	µg/mL	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL			
ACENAPHTHYLENE				16.8									
ANTHRACENE				6.2									
BENZO(A)ANTHRACENE	1.024	0.94	28.672	20.6	25	NA	24.22	18	21.96	22.41	3.260	4	14.8%
BENZO(K)FLUORANTHENE	1.12	0.85	31.36	25.4	25	20	32.15	41	28.71	25.4	8.116	5	28.3%
BENZO(A)FLUORENE	0.864	0.54	24.192	NA	NA	NA	NC	18	-	-	-	1	-
BENZO(A)PYRENE	0.824	0.76	23.072	17.7	25	10	20.33	14	17.41	17.7	5.761	5	33.1%
CHRYSENE	0.816	0.73 #	22.848	21.2	24	NA	18.72	16 #	19.98	19.96	3.419	4	17.1%
DIBENZO(A,C)ANTHRACENE	0.816	0.67	22.848	NA	36	NA	NC	12	24.00	-	16.971	2	70.7%
DIBENZO(A,H)ANTHRACENE				17.6	••								
FLUORANTHENE				3.3									
FLUORENE				13.1									
INDENO(1,2,3-C,D)PYRENE	0.872	0.90	24.416	10.2	26	15	30.78	12	18.80	15	9.083	5	48.3%
PHENANTHRENE	0.92	0.70	25.76	28.0	23	27	22.77	23	24.75	23	2.533	5	10.2%
PYRENE	1.2	1.02	33.6	29.8	32	11	33.60	26	26.48	29.8	9.111	5	34.4%

TABLE 3 - Results for IADN3 and IADN3a

AMPOULE/LAB CODE	IADN3	9225	IADN3a	9221	9222	9223	9224	9226	MEAN	MEDIAN	SD	n	%RSD
PARAMETER	µg/mL	µg/mL	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL			
ACENAPHTHENE						2	1.56						
ACENAPHTHYLENE	1.02	0.77	204	178	207	209	187.99	180	192.40	187.99	14.742	5	7.7%
ANTHANTHRENE	1.08	NA	216	NA	NA	NA	243.88	140	191.94	-	73.454	2	38.3%
ANTHRACENE				4.4									
BENZO(E)PYRENE	0.99	1.03	198	272	NA	NA	183.13	210	221.71	210	45.578	3	20.6%
FLUORANTHENE	1.51	1.10	302	295	257	136	299.48	280	253.50	280	67.744	5	26.7%
FLUORENE	1.28	1.12	256	223	272	232	233.61	220	236.12	232	20.872	5	8.8%
PHENANTHRENE				6.4									

TABLE 4 - Results for IADN4 and IADN4a

AMPOULE/LAB CODE	IADN4	9225	IADN4a	9221	9222	9223	9224	9226	MEAN	MEDIAN	SD	n	%RSD
PARAMETER	µg/mL	µg/mL	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL			
ACENAPHTHENE	1.056	0.75	29.568	21.4	25	25	18.35	22	22.35	22	2.787	5	12.5%
ANTHRACENE	0.968	0.66	27.104	16.4	23	NA	24.85	14	19.56	19.7	5.187	4	26.5%
BENZO(B)FLUORANTHENE	0.968	0.75	27.104	27.2	30	10	26.04	42	27.05	27.2	11.445	5	42.3%
BENZO(B)FLUORENE	1.208	0.95	33.824	NA	NA	NA	NC	26					
DIBENZO(A,H)ANTHRACENE	1.144	0.75	32.032	19.8	32	NA	25.94	17	23.69	22.87	6.683	4	28.2%
TRIPHENYLENE	1.016	0.89 #	28.448	44.7 #	##	NA	30.74	20 #	31.81	30.74	12.385	3	38.9%
CHRYSENE					40 ##								

TABLE 5 - Analytical Conditions

Lab Code	9221	9222	9223	9224	9225	9226
Ampoule Solvent	Toluene	Hexane	Iso-octane	Acetonitrile	Toluene	Benzene
Instrument/ Detector	GC/MSD: HP5890/HP5970	GC/MSD: HP5890/HP5970B	GC/MSD: HP5970	HPLC/Fluorescent/UV: HP1090/HP1046A/HP1050	GC/MSD: HP5890A/HP5970	GC/MSD: HP
Stationary & Mobile Phase	DB-5, 30 m	DB-5, 30 m	DB-5, 30 m	Reverse-phase gradient ($ACN/H_2O/C_{18}$); 16 cm X 4.6 mm; 5 µm particle size	DB-5, 60 m	DB-5, 30 m

TABLE 6 - Distribution of Participants' Results

Range of Target	9225		9221		9222		9223		9224		9226	
< 60%	0	0.0%	2	6.3%	0	0.0%	9	45.0%	0	0.0%	6	15.0%
60-75%	11	28.9%	7	21.9%	0	0.0%	3	15.0%	10	29.4%	10	25.0%
75-90%	17	44.7%	11	34.4%	12	37.5%	5	25.0%	16	47.1%	16	40.0%
90-110%	10	26.3%	7	21.9%	14	43.8%	3	15.0%	5	14.7%	5	12.5%
110-130%	0	0.0%	2	6.3%	2	6.3%	0	0.0%	1	2.9%	1	2.5%
> 130%	0	0.0%	3	9.4%	4	12.5%	0	0.0%	2	5.9%	2	5.0%

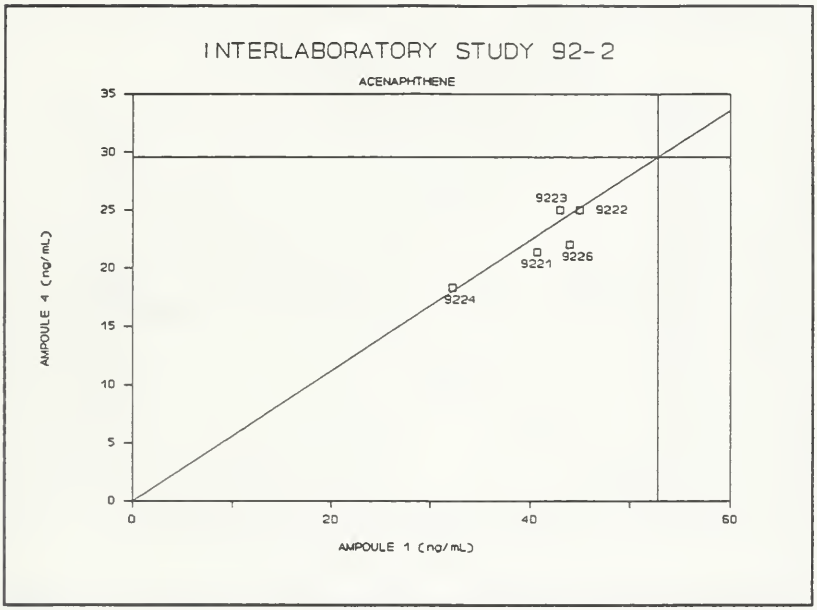

Figure 1 - Acenaphthene (IADN1a & IADN4a)

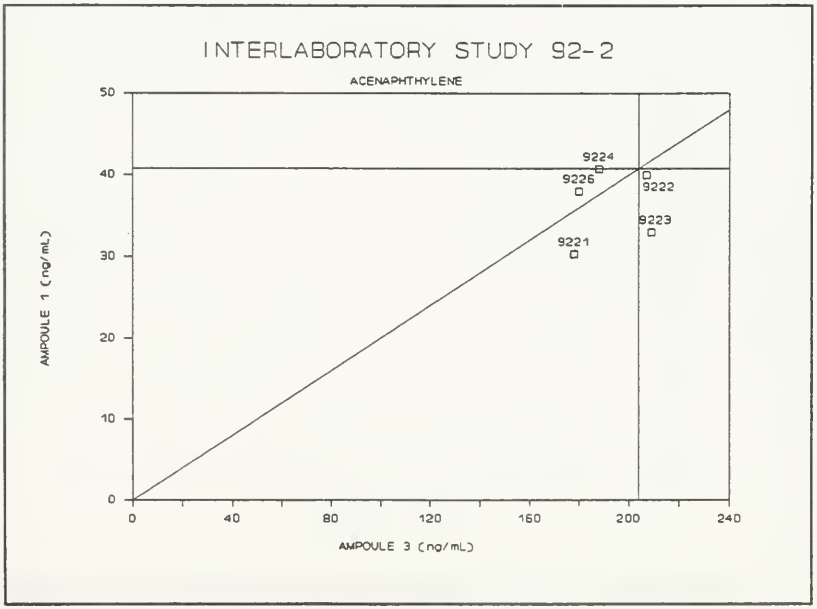

Figure 2 - Acenaphthylene (IADN1a & IADN3a)

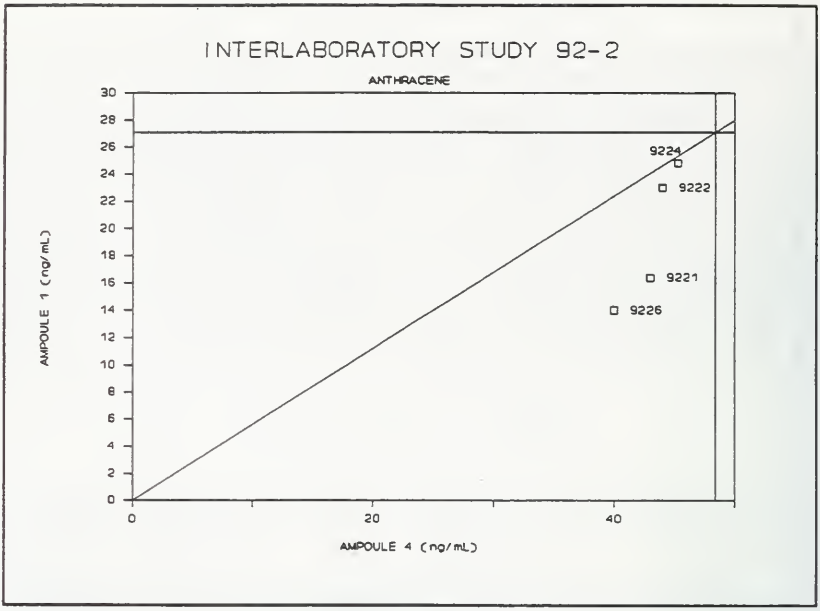

Figure 3- Anthracene (IADN1a & IADN4a)

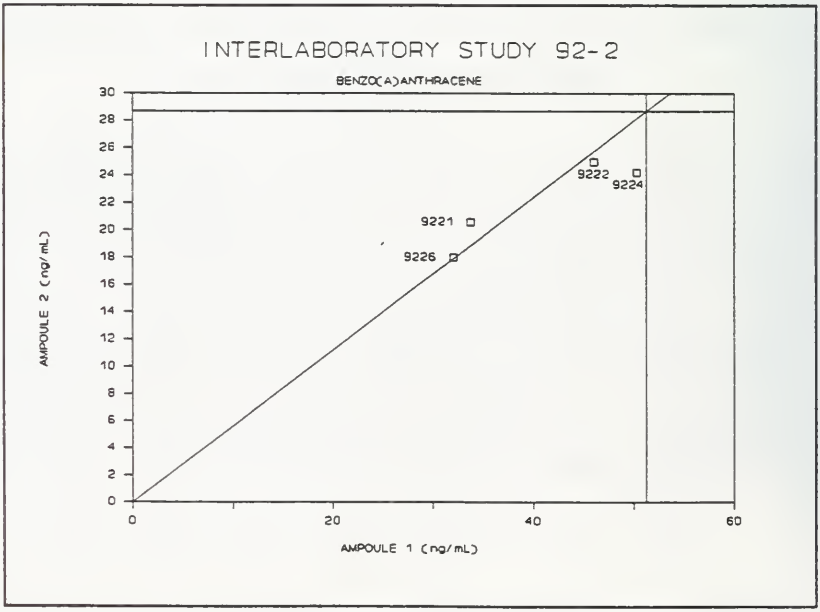

Figure 4 - Benzo(a)anthracene (IADN1a & IADN2a)

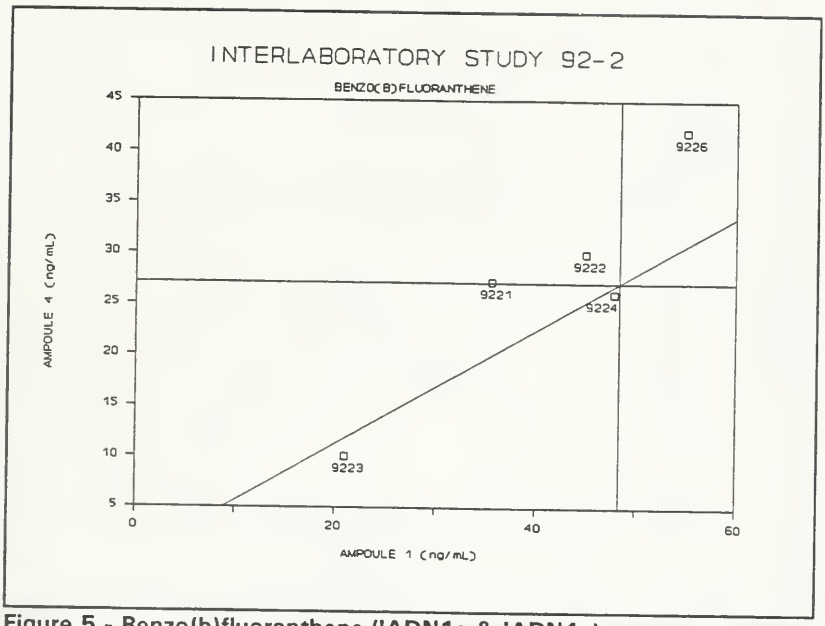

Figure 5 - Benzo(b)fluoranthene (IADN1a & IADN4a)

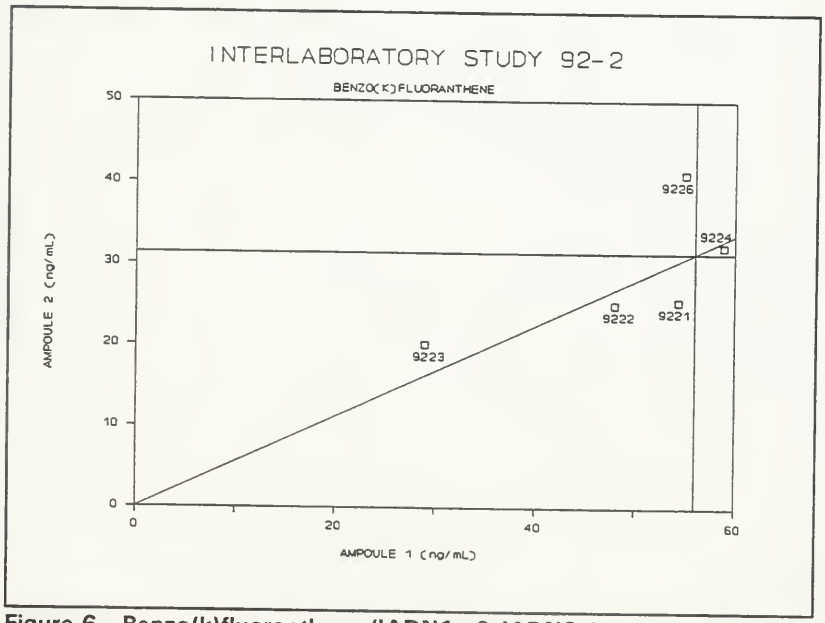

Figure 6 - Benzo(k)fluoranthene (IADN1a & IADN2a)

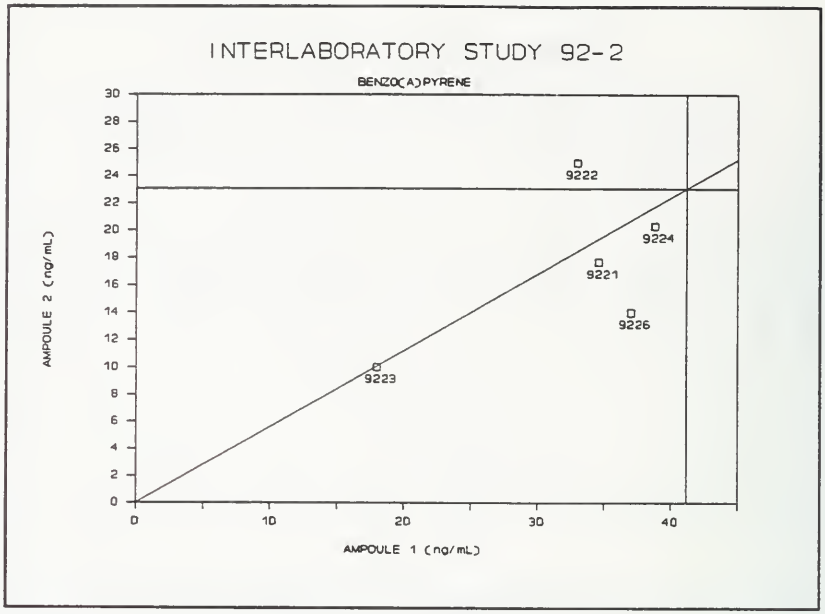

Figure 7 - Benzo(a)pyrene (IADN1a & IADN2a)

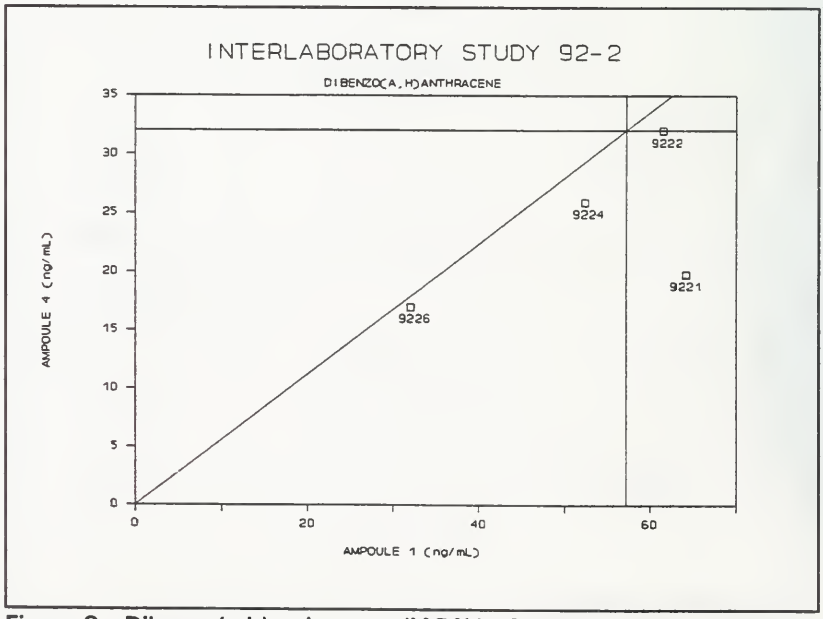

Figure 8 - Dibenzo(a,h)anthracene (IADN1a & IADN4a)

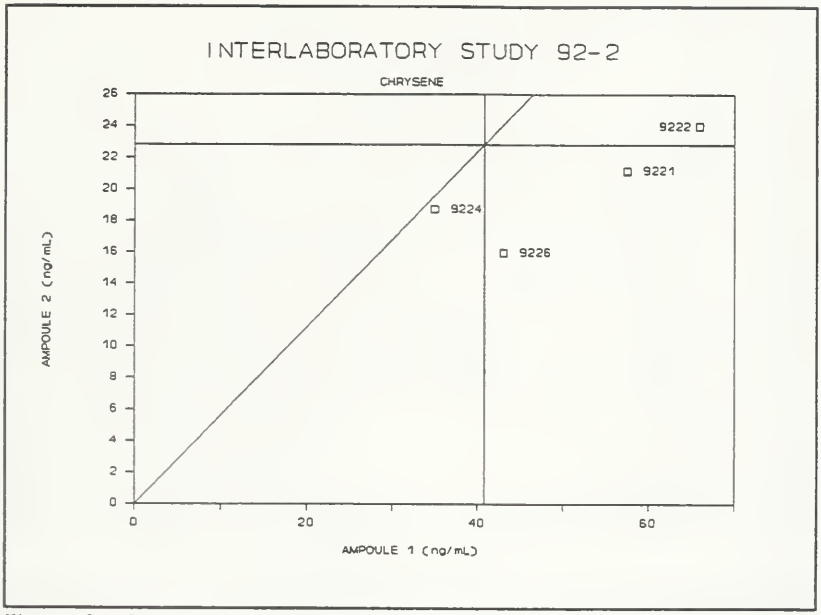

Figure 9 - Chrysene (IADN1a & IADN2a)

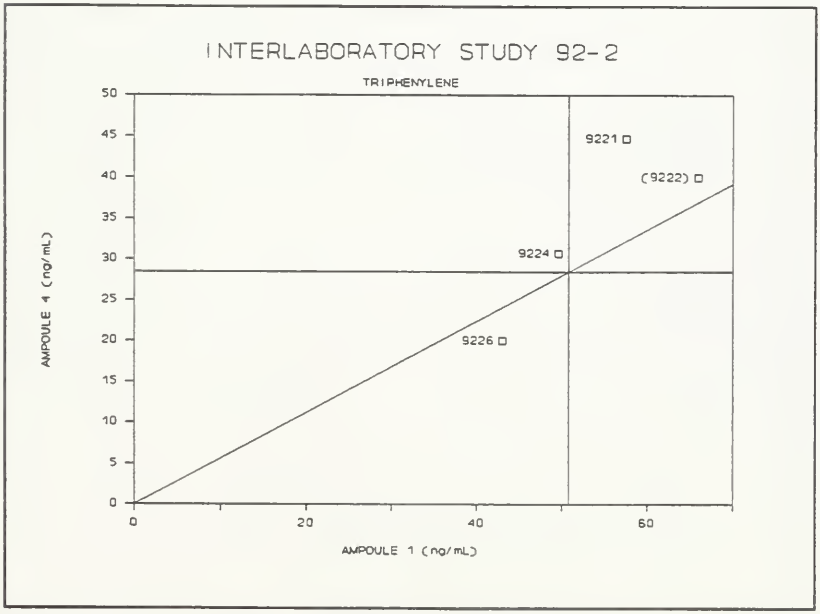

Figure 10 - Triphenylene (IADN1a & IADN4a)

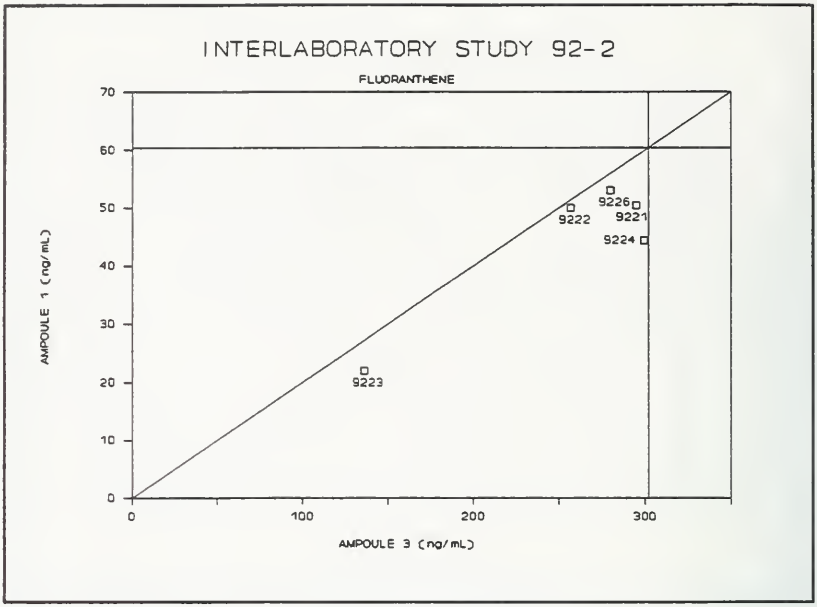

Figure 11 - Fluoranthene (IADN1a & IADN3a)

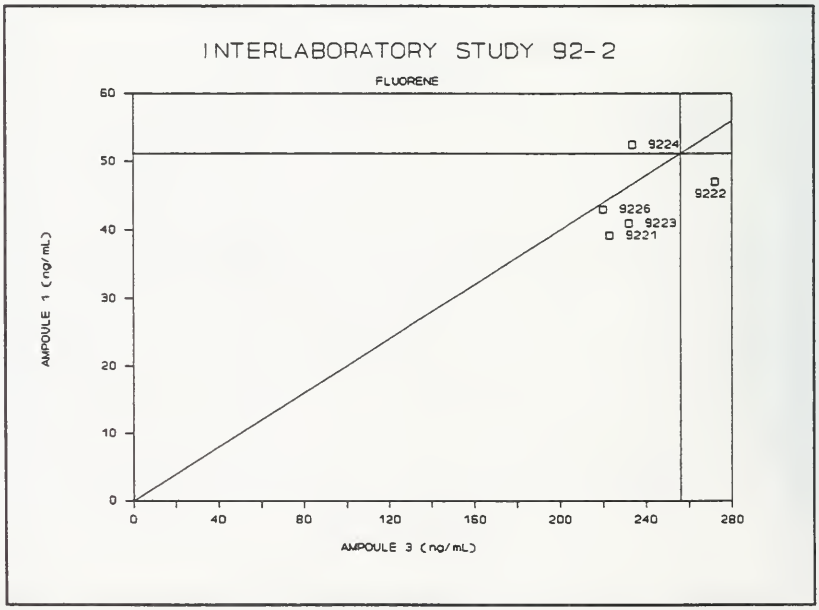

Figure 12 - Fluorene (IADN1a & IADN3a)

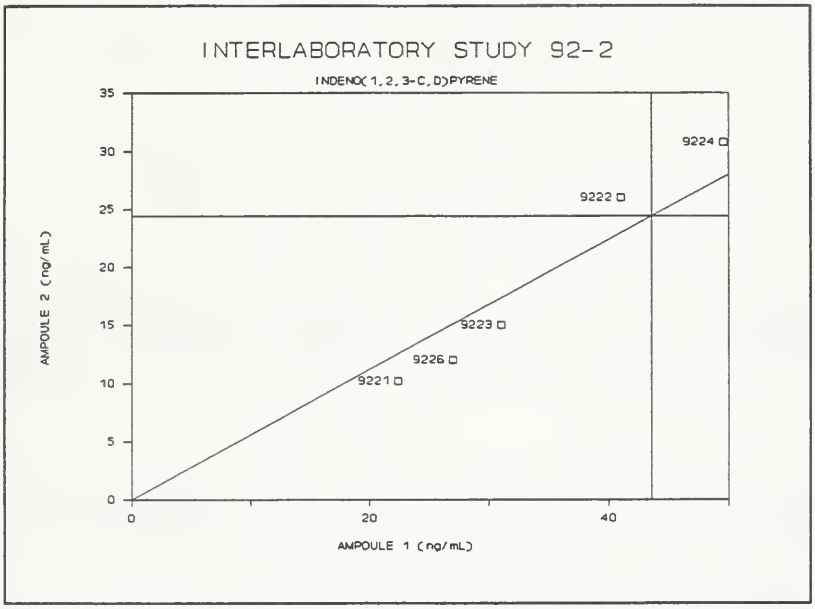

Figure 13 - Indeno(1,2,3-c,d)pyrene (IADN1a & IADN2a)

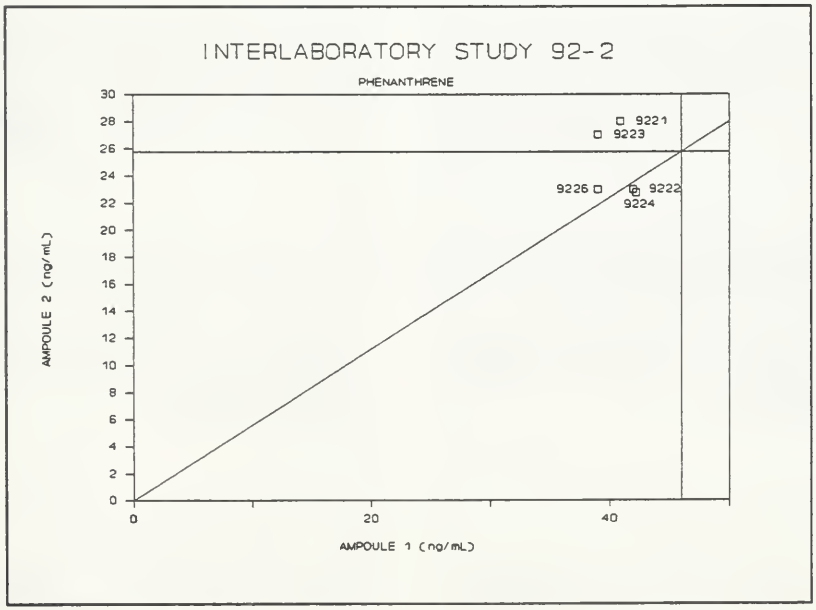

Figure 14 - Phenanthrene (IADN1a & IADN2a)

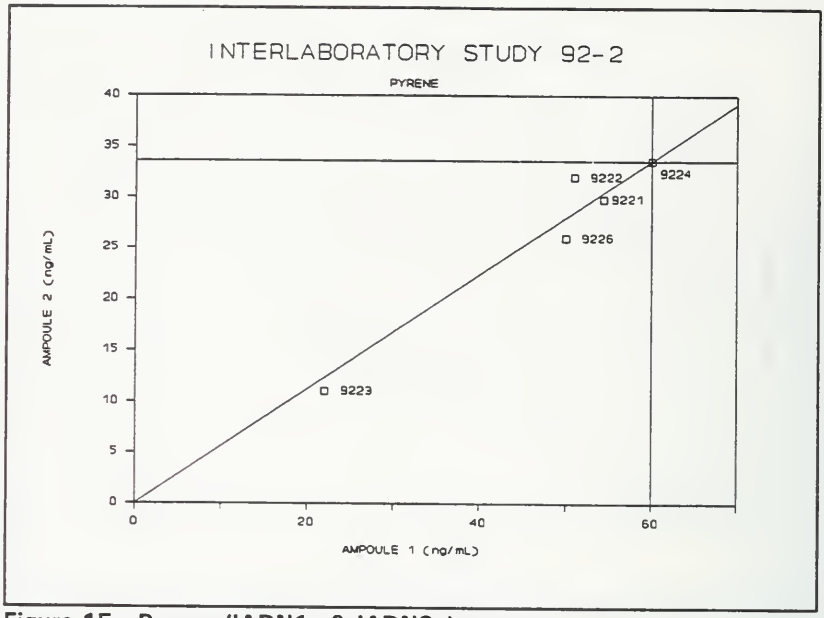

Figure 15 - Pyrene (IADN1a & IADN2a)

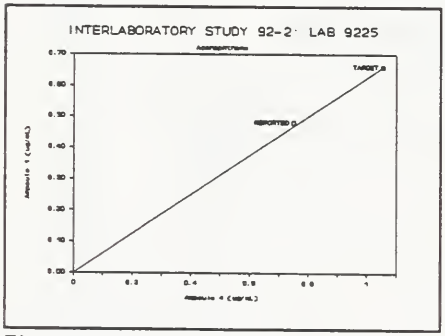

Figure 16 - Laboratory 9225: Acenaphthene

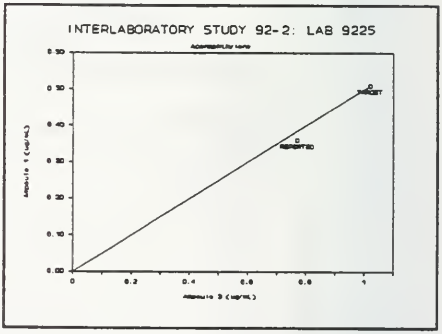

Figure 17 - Laboratory 9225: Acenaphthylene

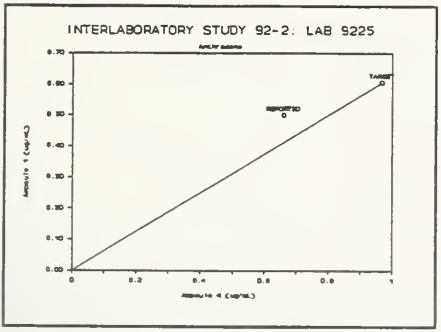

Figure 18 - Laboratory 9225: Anthracene

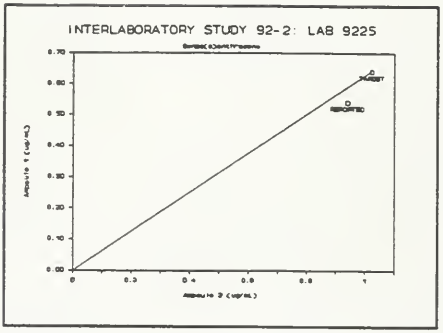

Figure 19 - Laboratory 9225: Benzo(a)Anthracene

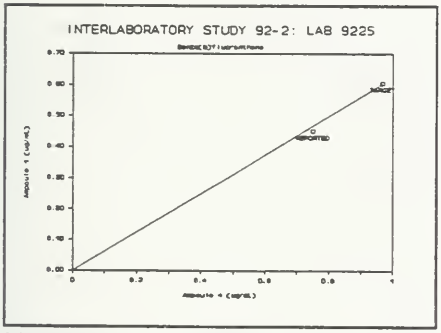

Figure 20 - Laboratory 9225: Benzo(b)Fluoranthene

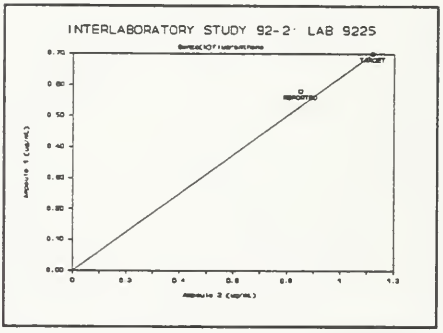

Figure 21 - Laboratory 9225: Benzo(k)Fluoranthene

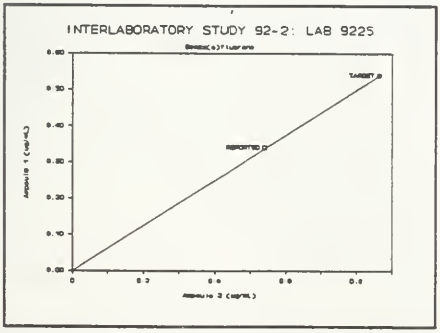

Figure 22 - Laboratory 9225: Benzo(a)Fluorene

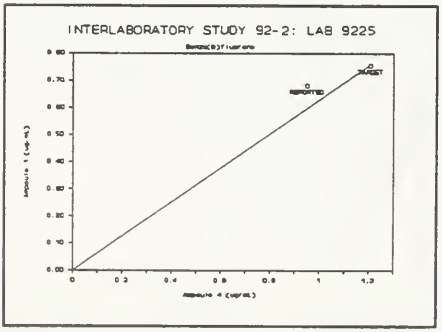

Figure 23 - Laboratory 9225: Benzo(b)Fluorene

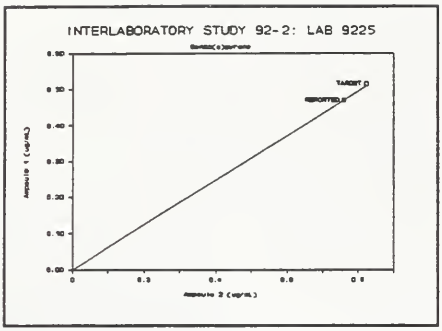

Figure 24 - Laboratory 9225: Benzo(a)Pyrene

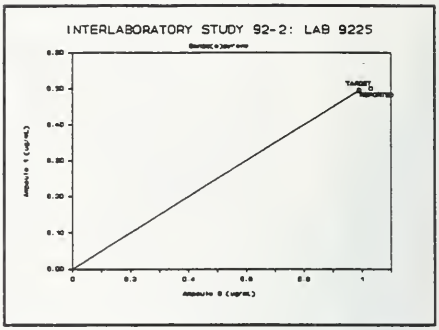

Figure 25 - Laboratory 9225: Benzo(e)Pyrene

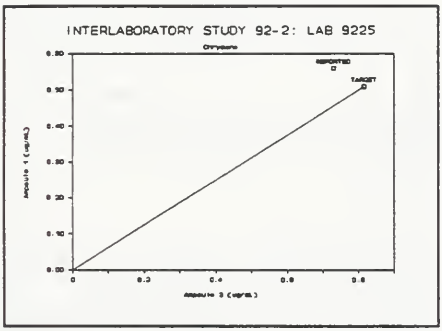

Figure 26 - Laboratory 9225: Chrysene

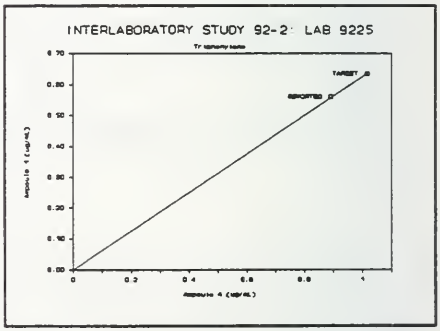

Figure 27 - Laboratory 9225: Triphenylene

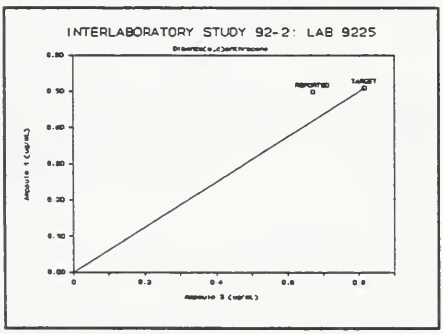

Figure 28 - Laboratory 9225: Dibenzo(a,c)Anthracene

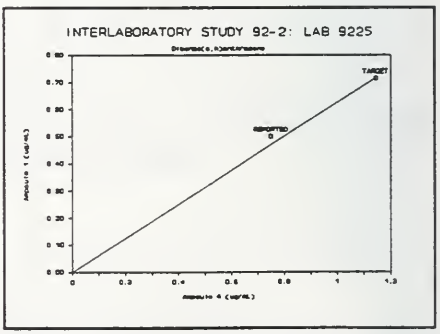

Figure 29 - Laboratory 9225: Dibenzo(a,h)Anthracene

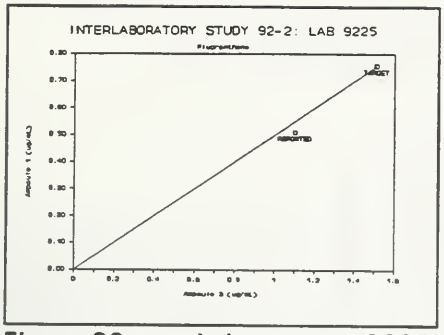

Figure 30 - Laboratory 9225: Fluoranthene

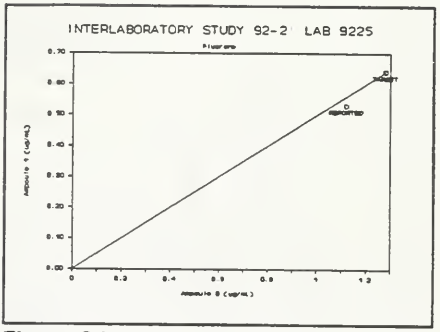

Figure 31 - Laboratory 9225: Fluorene

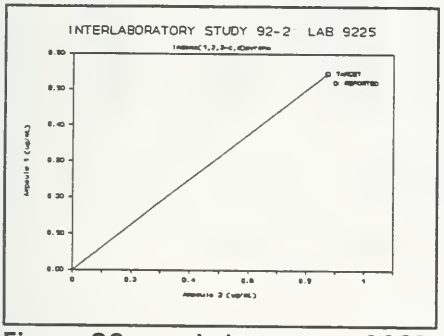

Figure 32 - Laboratory 9225: Indeno(1,2,3-c,d)Pyrene

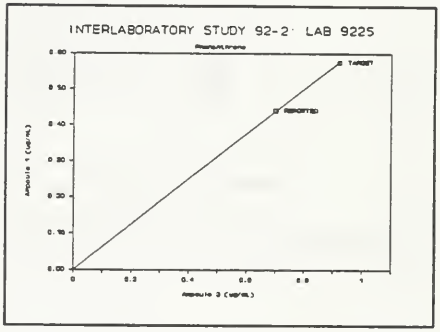

Figure 33 - Laboratory 9225: Phenanthrene

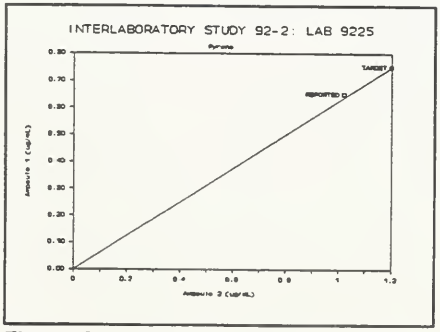

Figure 34 - Laboratory 9225: Pyrene

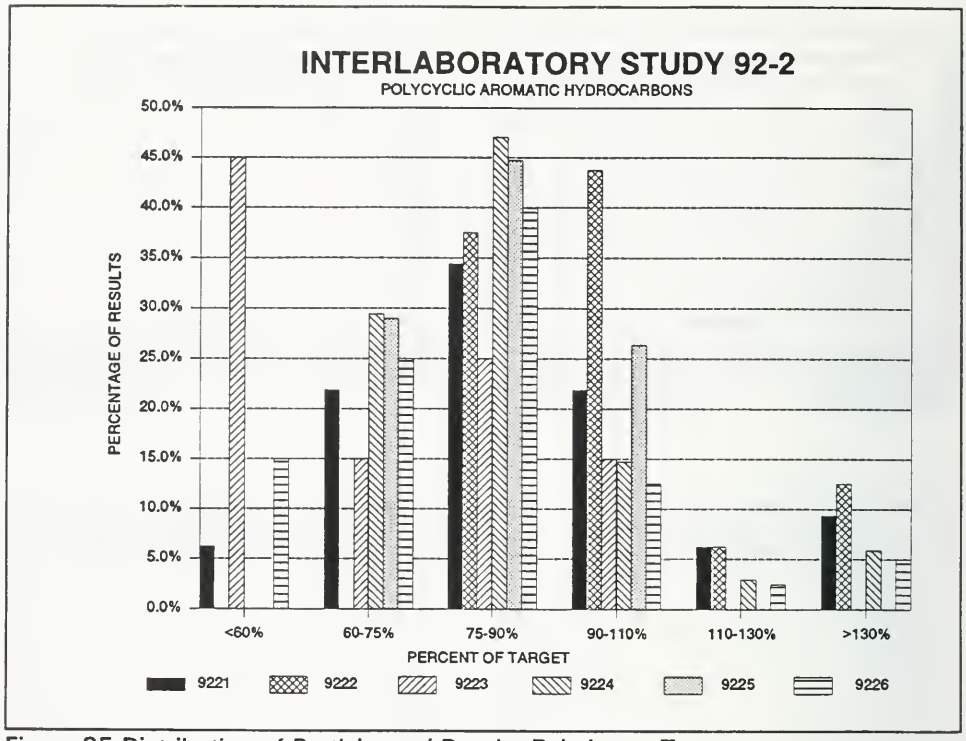

Figure 35 Distribution of Participants' Results Relative to Target

8 APPENDIX 2 - PARTICIPANTS AND CORRESPONDENCE

List of Participants

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Chung Chiu
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Environmental Technology Centre
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Gloucester, Ontario
K1G 3N3
(613) 990-8560

Quality Management Office

September 21, 1992

Dear Interlaboratory Study 92-2 Participant,

Please find enclosed four 5 mL ampoules for the analysis of Polynuclear Aromatic Hydrocarbons (PAH's). The ampoules are labelled IADN1, IADN2, IADN3, and IADN4 and indicate the solvent. If you are missing any of the ampoules or they have broken in transit, please contact me at (416) 235-5842 immediately for replacement.

The ampoules are ready for direct instrumental analysis. Break open the ampoule on the scored mark and transfer the contents to the appropriate sample container for your analytical system. No dilutions should be required, but if you do so, please mark the dilution factor used on the accompanying report form. The parameters present are indicated on the form.

Please report all results on the accompanying form by October 9, 1992.

Thank you for your participation in this study.

Your identification code is:

Sylvia Cussion
Laboratory Quality Audit Scientist
(416) 235-5842
FAX (416) 235-6110

INTERLABORATORY STUDY 92-2

PAH's FOR THE INTEGRATED ATMOSPHERIC DEPOSITION NETWORK

Identification Code:

Units:

PARAMETER	IADN1	IADN2	IADN3	IADN4
ACENAPHTHENE				
ACENAPHTHYLENE				
ANTHANTHRENE				
ANTHRACENE				
BENZO(A)ANTHRACENE				
BENZO(B)FLUORANTHENE				
BENZO(K)FLUORANTHENE				
BENZO(A)FLUORENE				
BENZO(B)FLUORENE				
BENZO(A)PYRENE				
BENZO(E)PYRENE				
CHRYSENE				
DIBENZO(A,C)ANTHRACENE				
DIBENZO(A,H)ANTHRACENE				
FLUORANTHENE				
FLUORENE				
INDENO(1,2,3-C,D)PYRENE				
PHENANTHRENE				
PYRENE				
TRIPHENYLENE				

INSTRUMENT AND DETECTOR USED FOR ANALYSIS:

125 Resources Rd.
Etobicoke, Ontario, M9P 3V6
Phone: (416) 235-5842
FAX: (416) 235-6110

January 4, 1993

TO: PARTICIPANTS OF INTERLABORATORY STUDY 92-2

Thank you for your participation in Interlaboratory Study 92-2 for the analysis of Polynuclear Aromatic Hydrocarbons (PAH's) in ampouled standards. This study was in support of the Integrated Atmospheric Deposition Network (IADN) program. I apologize for the delay in reporting results, but one participant did not report their final results until last week.

The results are provided in the attached tables. Target values are provided. Please inform me of any transcription errors by January 15, 1993.

Due to the variation in analytical methods among the participants, the following procedure was used to prepare the ampoules standards. A concentrated stock solution of each individual PAH was prepared in toluene. A combined solution was prepared in toluene, sealed into ampoules and labelled IADN 1-4. Due to their analytical working range, a set of these ampoules were provided to laboratory 9225. For the remaining participants, a further dilution was made in the specified solvent. The dilute solutions were ampouled and labelled IADN 1a - 4a. Each remaining participant received a set of the "a" series of ampoules in the solvent specified by them.

The Quality Assurance Working Group of the Canada-Ontario Agreement (COA) has been the directing force for these interlaboratory studies. They wish to know the identities of the participating laboratories for the purposes of data comparison for IADN. The Program Managers and Principle Investigators (U.S. and Canadian) for IADN also wish to have the laboratories identified. As the original invitation for this study indicated that laboratory codes were confidential, I am asking each participant to give me permission to reveal their identities to these groups of data users. Please notify me in writing with your permission to reveal your study code.

A date has not yet been set for the next set of ampouled standards in this series of IADN studies, but hopefully will take place in late February or in March. A letter will be sent out giving several weeks notice.

Your identification code is:

Sylvia Cussion
Laboratory Quality Audit Scientist

125 Resources Rd.
Etobicoke, Ontario, M9P 3V6
Phone: (416) 235-5842
FAX: (416) 235-6107

January 15, 1993

TO: PARTICIPANTS OF INTERLABORATORY STUDY 92-2

Please find enclosed an updated Table 1 for Interlaboratory Study 92-2 (PAH's). Laboratory 9224 provided an updated result for Fluorene in this ampoule before the table of results went out to all of the participants. I apologize for the error and any inconvenience this may have caused.

Sylvia Cussion
Laboratory Quality Audit Scientist